AD-A122 109 LASER AUGMENTED REACTION RATES - APPLICATION TO INTERCONVERSION AND OXIDA..(U) CORNELL UNIV ITHACA NY DEPT OF CHEMISTRY S H BAUER ET AL. 15 NOV 82 DFT-3 1/1

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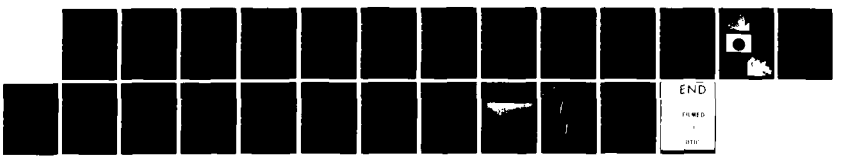

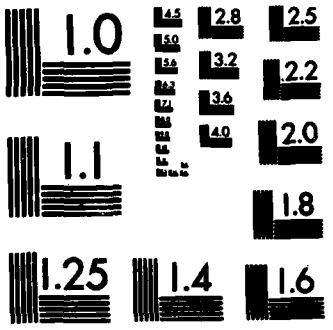

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REPORT DOCUMENTATION PAGE

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1. REPORT NUMBER: DET- 3	2. GOVT ACCESSION NO.: AD-A122109
3. RECIPIENT'S CATALOG NUMBER: - - -	
4. TITLE (and Subtitle): Laser Augmented Reaction Rates - Application to Interconversion and Oxidation of the Boranes	5. TYPE OF REPORT & PERIOD COVERED: FINAL 02/12/81 - 09/01/82
	6. PERFORMING ORG. REPORT NUMBER:
7. AUTHOR(s): S. H. Bauer - Professor (Emeritus); Peter M. Jeffers - Senior Research Assoc.	8. CONTRACT OR GRANT NUMBER(s): DAAG 29 81-K-0037; Project No. P-18139-C
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Department of Chemistry, Cornell University, Ithaca, New York 14853	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS:
11. CONTROLLING OFFICE NAME AND ADDRESS: U. S. Army Research Office, Post Office Box 12211, Research Triangle Park, NC 27709	12. REPORT DATE: 11/15/82
	13. NUMBER OF PAGES: —
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)	15. SECURITY CLASS. (of this report): Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE: —

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

NA

18. SUPPLEMENTARY NOTES

The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Chemiluminescent reaction
Borane adducts
Microwave production $O(^3P)$
Low pressure flames
Vibrational disequilibrium
Syntheses in μw plasmas

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The practical utility of low power microwave plasmas for affecting syntheses of useful products was further demonstrated during the first part of the report period. In a microwave discharge low-pressure flow-reactor, which was previously developed to convert mixtures of trimethoxyborane and hydrogen to the dimethoxy derivative, silicon tetrachloride reacted with hydrogen to generate polycrystalline silicon films. Silicon tetrafluoride

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can be similarly reduced. Also, very finely divided Si_3N_4 was produced from mixtures of $SiCl_4$, N_2, and H_2 when passed through this discharge.

The latter portion of the report period was devoted to the study of the chemiluminescence generated when borane adducts [H_3BX; $X=N(CH_3)_3$; $N(C_2H_5)_3$; CO; PYR; THF; $S(CH_3)_2$] were mixed with excess oxygen atoms (^3P). A low pressure flame (at 2-20 torr total --- mostly He) developed. Its spectrum was quantitatively recorded and fully analyzed. The most prominent band system was the extensive α bands of BO. The trimethylamine adduct produced the highest intensity and showed a few bands of electronically excited BH, NH, CH, and CN in addition to the α bands, as well as several β system bands of BO. The rotational temperatures indicated by these bands were approximately 350°K but the vibrational distribution in the upper electronic state is clearly non-Boltzmannian. Selected state populations (v'=4 to 8) indicated temperature of approximately 3000°K. The experimental program was terminated prior to the development of a detailed mechanism for this overall conversion. The only reaction which is sufficiently exoergic to generate BO ($A^2\Pi$) is the abstraction of a boron atom by an oxygen atom from BH.

Alpha

INTERCONVERSION AND OXIDATION OF BORANES

FINAL REPORT

S. H. BAUER AND P. M. JEFFERS

NOVEMBER 15, 1982

U. S. ARMY RESEARCH OFFICE

CONTRACT NO.: DAAG 29 81-K-0037

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PART I

SYNTHESES IN A LOW POWER MICROWAVE DISCHARGE II --- POLYCRYSTALLINE SILICON AND AMORPHOUS SILICON NITRIDE

INTRODUCTION

In a previous communication (1), we reported on the partial reduction of trimethoxyborane by hydrogen when mixtures of these gases were passed through a low power microwave [S band] discharge. Here we describe experiments with mixtures of $SiCl_4/H_2$, SiF_4/H_2 and $SiCl_4/N_2/H_2$. Indeed, microwave discharge conditions proved to be particularly effective for producing elementary polycrystalline silicon from the tetrahalides, and amorphous Si_3N_4 from the mixtures which incorporated N_2. The mechanisms have yet to be determined.

EXPERIMENTAL

The flow system used has been described (1). The silicon tetrachloride was stored as a liquid at 20°C, and flow of its vapor was adjusted by a needle valve through an appropriate meter. Gaseous SiF_4 was metered from a storage bulb at one atmosphere. Experimental details are listed in Table 1. Gaseous reaction products were trapped at -196° and were subsequently analyzed by infrared absorption spectra and mass spectrometry. With $SiCl_4/H_2$ (or SiF_4/H_2) mixtures a dark red-brown metallic-like deposit formed at the position of the microwave discharge heads. The solid readily plated out onto glass, mica or metal screens which were appropriately supported in the flow tube. Samples were thus deposited directly onto copper grids for electron microscopic examination. Mixtures of $SiCl_4/H_2/N_2$ yielded a gray light-brown powder which was scraped off the flow tube wall, again immediately at the discharge head position. It also was analyzed by electron microscopy. $SiF_4/N_2/H_2$ mixtures

also generated a powder, somewhat darker than that with $SiCl_4$; no electron micrographs were taken.

In runs A through F, and run P, the gaseous products were trapped at -196°C, then expanded into a 250 ml bulb, and the pressure recorded. Runs X and C were made under nearly identical flow conditions. The assumption that all the gaseous products in C were HCl and $SiCl_4$ (identified by mass spec and IR) implies that 80% of the $SiCl_4$ was converted. [The mass spectral peak intensities indicated 85% conversion, whereas from the IR intensities we estimated 75% conversion in run C.] In all runs A-F and P the measured product pressures were 2.5-3 times those expected had there been no conversion. For runs G an H, the products were fractionately distilled into calibrated volumes; the recorded pressures indicated 59% and 52% conversion, respectively.

GENERAL OBSERVATIONS

Quantitative estimates by pressure, infrared absorption, and mass spectra of the trapped reaction products indicated that 50-80% of the initial $SiCl_4$ had reacted. When hydrogen was used as the carrier gas, solid silicon and HCl were the primary products. The other major component in the trap proved to be unreacted $SiCl_4$; small amounts of $HSiCl_3$ were detected by IR. In addition, small amounts of HCN were found along with at least one other unidentified minor product for which a lone peak appeared in the infrared spectrum. This could not be assigned to any anticipated species. The product gases from mixtures of SiF_4/H_2 were H_nSiF_{4-n}, with n=1,2,3. Too few runs were made

with SiF_4 to permit the unscrambling of the product distribution, and its dependence of flow rates and power input.

The flow tubes were horizontal and the deposited silicon appeared predominantly on the upper tube surface, immediately above the plasma region. Glass and metal supports held in the discharge area were readily coated. Electron microscopy showed fiber-like growth on the copper grid (Fig. 1). Its diffraction pattern was entirely that of crystalline silicon (Fig. 2). [This was confirmed by an X-ray analysis of our samples at the laboratory of Dr. Eli Yablonovitch (Exxon).] The gray powder generated in $SiCl_4/H_2/N_2$ flows --- no dark brown deposit was observed for these mixtures --- was scraped off the tube wall and transferred onto a copper grid for electron microscopy, which showed approximately uniform spherical particles, about 500Å in diameter (Fig. 3). These gave a strictly amorphous diffraction pattern.

The source of the carbon for HCN formation is uncertain. It may have come from the pyrolysis of dioctylphthalate vapors, carried over from the oil filled flow meter. Henis, So and Miller (2) reported useful nitride formation in radio frequency flow discharges of alkenes with C_2N_2. The production of HCN and C_2N_2 from highly excited hydrocarbon/N_2 mixtures is not unexpected; intense CN emission was readily generated by shock heating such mixtures to temperatures above 2000°K (3). The reduction of the silicon tetrahalides with either hydrogen or hydrogen/nitrogen mixtures proceeded smoothly, with 50-80% conversion in all instances. In contrast to the reduction of

trimethoxyborane (1), high microwave powers generated better yields.

CONCLUSIONS

The direct reduction of $SiCl_4$ with H_2 and the reaction of $SiCl_4$ with N_2/H_2 mixtures, induced in a microwave plasma, may compare favorably and economically with current commercial processes [contrast Sarma and Rice (4)]. Clearly, the level of impurities in this synthetic route is determined by the impurities in the feed material; the quartz reactor introduces no undesired species, and the electrodes are external. In contrast to other techniques under development which are energy intensive, the state-of-art in klystron design has led to efficient conversion of electrical input to microwave radiation (≈60%). Furthermore, proper electrode design and pressure control should provide optimum coupling between the power unit and the plasma.

ACKNOWLEDGMENTS

This investigation was supported by the ARO under Grant No. DAAG29-81-K-0037. We sincerely thank Dr. E. Yablonovitch for providing us with the X-ray data.

TABLE 1 - Operational Details

Run	Flow Rates (mole/min) x 10^5 SiX_4	H_2	N_2	Power (watts)	Comments
A	2.0($SiCl_4$)	40		10	IR, M.S. + mostly HCl
B	2.9 "	55		8	IR shows some $HSiCl_3$, large HCl
X	2.4 "	55		0	P($SiCl_4$, collected in 5 min) = 9.5 torr
C	2.4 "	55		25	P(products, collected in 5 min) = 32.5 torr $HSiCl_3$ seen in IR, but small in M.S.
D	3.1 "	10	40	20	IR; trapped product show good yield of HCl; gray powder formed. HCN seen by IR, M.S. no $HSiCl_3$ found.
E	3.0 "	5	45	20	
F	6.0 "	20	20	20	
G	3.9 "	48		20	63.5 torr HCl, 11 torr $SiCl_4$
H	7.8 "	100		30	57 torr HCl, 13 torr $SiCl_4$
I	2.2(SiF_4)	12		25	Si; deposit as with ($SiCl_4$ + H_2).
J	3.0(SiF_4)	6	9	25	No Si deposit; IR shows little reaction (Si_3N_4?).
K	2.0($SiCl_4$)	30		15	IR - mostly HCl
L	5.8 "	50(He)		15	No Si deposit. IR shows large $SiCl_4$; small HCl
M	2.5 "	50		20	Good yield of Si and HCl; some $HSiCl_3$ (IR)
N	2.5 "	50		30	IR shows HCl, $HSiCl_3$. X-ray grids coated
O	3.9 "	77		30	IR shows HCl, $HSiCl_3$. X-ray grids coated
P	2.4 "	48		25	Pyrex fibers coated for X-ray analysis.

FIGURE LEGENDS

Figure 1. An electron micrograph of Si crystallites taken at a magnification of 7300.

Figure 2. Electron diffraction pattern produced by the above sample.

Figure 3. An electron micrograph of Si_3N_4 powder at a magnification of 20,000.

Figure 1.
An electron micrograph of Si crystallites, taken at a magnification of 7300.

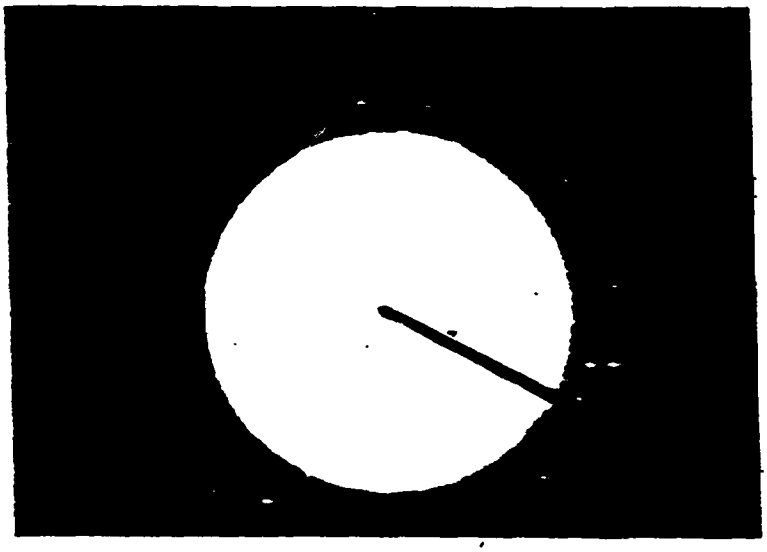

Figure 2.
Electron diffraction pattern produced by the above sample.

Figure 3.
An electron micrograph of Si_3N_4 powder, at a magnification of 20,000.

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PART II

CHEMILUMINESCENCE GENERATED IN THE REACTION BETWEEN BORANE ADDUCTS AND ATOMIC OXYGEN

(Outline of Manuscript in Preparation)

INTRODUCTION

In a rapid-mixing fast-flow tube reactor, Anderson and Bauer ured the rates of attack on B_2H_6 and H_3BCO by O and N atoms, as as by N_2O, NO, NO_2, and O_2. The products of reaction were yzed by a direct sampling TOF mass spectrometer. In a parallel reactor (quartz tube), the emitted chemiluminescence was re- led photographically. From these data both the stoichiometry the exoergic pathways required to generate the highest recorded uencies were determined. To account for these observations two iation mechanisms (which operate concurrently) were required:

Mechanism 1: $O + H_3BCO \rightarrow OH + [H_2BCO]^* \rightarrow OH + BH_2 + CO$

$\rightarrow H_2O + [HBCO]^* \rightarrow H_2O + BH + CO$

Mechanism 2: $O + H_3BCO \rightarrow [H_3BO]^* + CO \rightarrow BO + H_2 + H + CO$

+ other compounds, with oxygen attached to boron.

highly exoergic steps, which generate BO*, are presumed to arise the attack by $O(^3P)$ on BH or on BH_2.

In a subsequent investigation Jeffers and Bauer measured the ation rate of the amino-borane adducts: $H_3BN(CH_3)_3$ and $(C_2H_5)_3$ by O atoms. These rates are about two orders of magni- faster than for borane carbonyl and four orders of magnitude er than for B_2H_6. The present report concerns the chemilumi- ence generated when oxygen atoms attack these and other adducts

of BH_3 [NC_5H_5(pyridine); NH_2(t-but); $S(CH_3)_2$; and OC_4H_8(THF)].

GENERAL OBSERVATIONS

The most intense flames were produced by the adducts of the trialkylamines. This is only partly due to their higher vapor pressures which are available at room temperature. The distribution of intensities for the various (v';v") bands of the $BO^*(A^1\Pi \rightarrow X^1\Sigma^+)$ transition appears to depend on the base attached to the BH_3 moiety. However, our impressions are based solely on photographic spectra. Whereas the polaroid paper we used to record these has a very high sensitivity, it can be notoriously misleading relative to measures of intensity. Since the most intense radiation is generated by $H_3BN(CH_3)_3$, we have devoted most of our efforts toward recording and analyzing the luminescent radiation emitted when low pressures of this adduct (in a helium carrier, at room temperature) are rapidly mixed with a stream of atomic oxygen.

We have restructured the experimental configuration and set up a 3/4 meter JA spectrometer with a photomultiplier detector to record the entire emission, from 2650 Å down to 6500 Å, at a resolution of approximately 0.7 Å. Careful calibration of the wavelength scale permitted us to assign about 44 bandheads. As a consequence of this time consuming effort we can state with certainty that superposed upon the very extensive α-system of BO, there are also some bands from the β-system, as well as moderate intensities of OH*, NH*, CH*; a weak BH* emission and a very strong CN*. To determine quantitatively the relative intensities of the bands in these systems proved more difficult than we had anticipated in view of the persistent irreproducibilities over the extended periods of time required

to record the entire spectrum. We discovered that the intensity levels of these bands are extremely sensitive to the NO titration end-point (Fig. 1), whereby we generate the atomic oxygen [$N_2 \xrightarrow{\mu w} 2N$; $N + NO \rightarrow N_2 + O$]. By setting up a low dispersion monochromator which views the integrated intensity of a selected band we have optimized the chemiluminescent intensities and used the output from this monochromator to monitor the level of titration. Thus, a set of reliable intensities are available, and we are able to estimate the rotational and vibrational temperatures of the freshly generated BO*. It is evident that the intensity distributions recorded in other laboratories for the BO emission generated from $B + O_2(N_2)$, etc.) $\rightarrow BO^* + O(N_2$, etc.) is significantly different from what we recorded for the chemiluminescence generated in the attack of boranes by oxygen atoms.

QUANTITATIVE RESULTS

The optical-amplifier-recorder train was calibrated for relative intensity measurements by recording the emission from a psuedo-black-body source, at the fixed geometry, from 260 to 600 nm. After correcting for the dependence of emissivity on the wavelength, for the tungsten source, the relative intensities of 44 bands, integrated over their rotational lines, were evaluated (Table I). These were then corrected for the corresponding Franck-Condon factors, and the relative populations in the various vibrational levels for the A state were estimated. By and large, the data from many runs check each other (scatter within 50%); variations as a function of the upper state vibrational quantum number match quite well (Fig. 2). These results are essentially independent of pressure over the range

2-20 torr. It appears that no single vibrational temperature exists. For example, the populations of the states v'=4,5,6,7 can be fitted by 2940°K (7/30/82) and by 3800°K (8/3/82), but the breaks between (3<v'<4) and (7<v'<8) are unmistakable in each of these runs.

The rotational temperatures were estimated by comparing computed band contours with those recorded. A typical example of a strong BO bands is shown in Fig. 3. It appears that all the bands have similar rotational line distributions and closely similar temperatures, ~350°K. Rotational equilibration is anticipated since at the ambient pressure in the flame (at 2 Torr) the excited species are subjected to at least 25 collisions per microsecond, while the lifetime of BO* is ~1.7 μs. A larger number of collisions occur at the higher pressures.

To determine whether a population inversion is generated in the production of BO the branching ratio for the partition of the nascent BO between the X and A states must be estimated. An attempt to use a line reversal measurement at the (4,0) bandhead was not successful because the Xe lamp source clearly had an equivalent black-body temperature at 353 nm which was lower than that of the flame.

The optical-amplifier-recorder train was recalibrated for absolute intensity measurements by recording the emission from the reaction $O + NO \rightarrow NO_2 + h\nu$, at the fixed geometry. Since the rate constant for this reaction has been determined it served as an actinometer for the flow system used in producing the BO* emission. Still, an imprecise correction had to be made for the relative volumes of the two flames. A lower limit derived in this manner for the number of photons generated per 10^3 B atoms injected is ≈5.

DISCUSSION

Several interesting puzzles remain to be solved relative to the above observations.

a) The most significant laboratory experiment would be to determine the branching ratio for the (A/X) states. This could be done by measuring the total BO concentrations via LIF, under carefully controlled gas flow rates and mixing conditions.

b) Detection and measurement of BH and BH_2 via LIF would provide data for the development of a more complete mechanism than that initially proposed by Anderson and Bauer.

c) In view of the observed low rotational temperature (hence low translational temperature) it remains for highly exoergic reactions to be the source of the highly excited electronic and vibrational emitters. Only two reactions involving B/H species have sufficient energy to account for the observed v'=10 in the A state:

$$BH + O \rightarrow BO^* + H \quad ; \quad BH_2 + O \rightarrow BO^* + H_2.$$

No mechanisms have yet been developed which account for the production of BO in the β-system. This requires considerably higher exoergicity. Also, we can cite no reactions which account for the other excited species. One possible explanation is the occurrence of extensive energy pooling among the excited species. Thus, if oxygen atoms attack $BH(A^1\Pi)$, then $BO(B^2\Sigma^+)$ could be produced.

d) If one accepts the above reactions for the production of BO* there still remains the puzzle as to the origin of the stepwise features in the vibrational state populations.

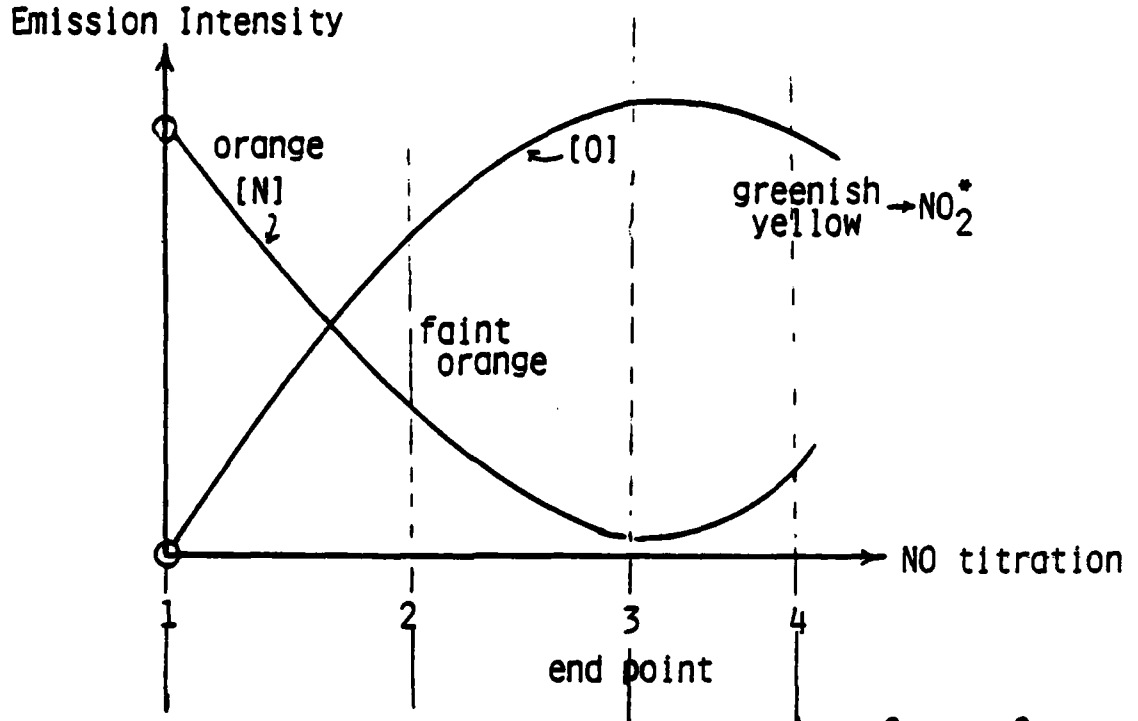
e) Is there chemiluminescence in the infrared? From the multiplicity of possible sources for OH, NH, etc. one should anticipate vibrational excitations to be prominent.

These data challenge both experimentalists and theoreticians. The need for further investigations is clearly indicated.

TABLE I

Band* Assignment	λ (Å)	Corrected Intensity	Band* Assignment	λ (Å)	Corrected Intensity
β(0,3)	2680	0.29	(6,3)	3980	1.46
β(1,4)	2720	0.44	(1,0)(4,2)	4050	5.75
β(2,5)	2760	1.23	(2,1)	4150	3.81
?	2820	2.42	CN	4215	3.81
?	2920	2.84	(0,0)(3,2)	4260	2.28
(9,0)	2950	1.66	CH	4315	1.51
?;(10,1)	2980	2.81	BH	4335	0.87
(8,0)	3045	3.19	(1,1)	4370	5.62
OH	3080	2.99	(5,4)	4510	1.70
(9,1)(7,0)	3120	7.52	(0,1)(3,3)	4615	4.63
(10,2)(8,1)	3225	6.83	(1,2)	4760	2.85
(6,0)	3270	4.28	(2,3)	4890	2.32
(9,2)(7,1)	3330	5.10	(0,2)	5050	5.73
NH	3360	2.40	?	5170	3.18
(5,0)	3390	7.00	?	5280	1.08
(6,1)	3470	3.26	(2,4)	5360	2.74
(4,0)	3530	9.99	?	5460	0.34
CN	3570	2.39	(3,5)(0,3)	5530	5.05
(5,1)	3620	2.33	?	5620	2.46
(3,0)	3680	6.21	(1,4)?	5750	5.04
(4,1)	3760	1.65	?	5870	5.25
CN{3790 3950	3870	95.45	?	5925	0.67

* If not designated with formula it is αBO*; β bands are specifically identified.



$H_3B{\cdot}N(CH_3)_3 + O(^3P)$	$N(CH_3)_3 + O(^3P)$	OH	3093	0	VS	S	W	$A^2\Sigma^+ \rightarrow X^2\Pi_i(0,0)$
		NH	3362	M	VS	S	0	$A^3\Pi_i \rightarrow X^3\Sigma^-(0,0)$
		CN	3580 3880	S	VS	M	0	$B^2\Sigma^+ \rightarrow X^2\Sigma^+$ (2,1) (0,0)
		CH	4314	VS	S	0	0	$A^2\Delta \rightarrow X^2\Pi(0,0)$
		BH	4333	S	VS	S	0	$A^1\Pi \rightarrow X^1\Sigma^+(0,0)$
		BO	3520 4261	0	VS	S	0	$A^2\Pi \rightarrow X^2\Sigma^+$ (4,0) (0,0)

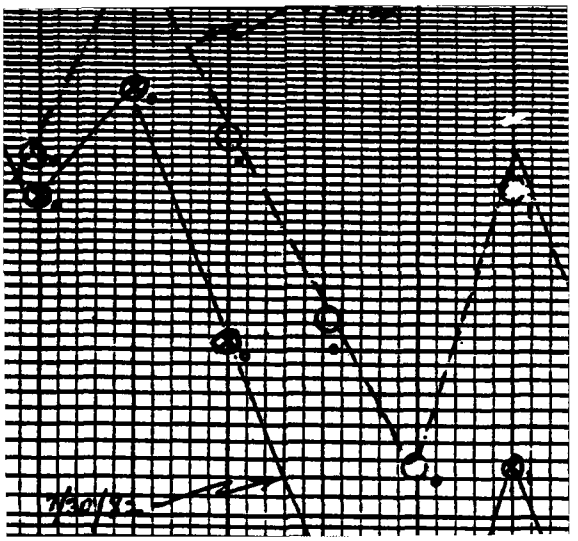

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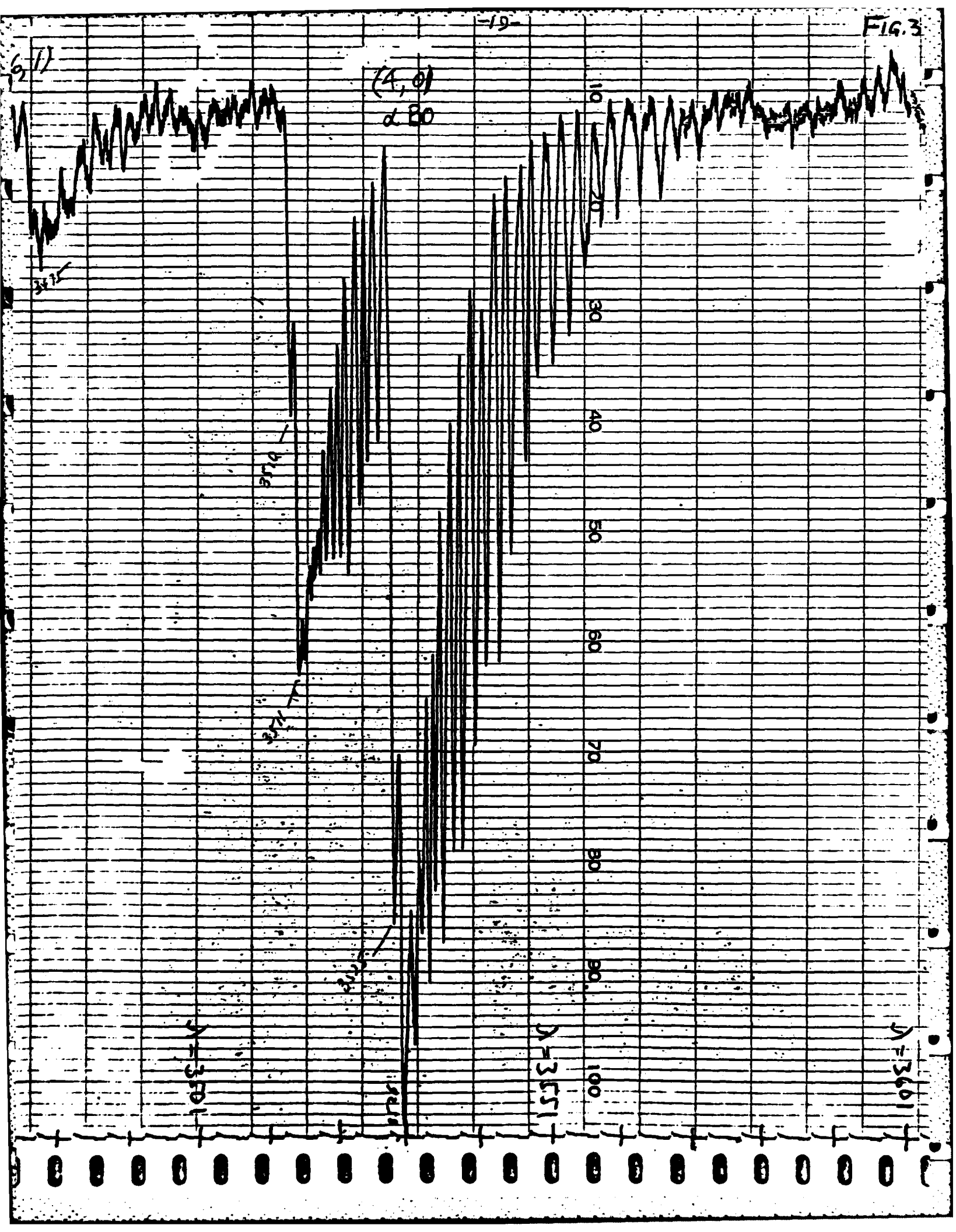
FIG. 3



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